Hydrogen adsorption on Ru(001) studied by Scanning Tunneling Microscopy

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Abstract

The adsorption of hydrogen on Ru(001) was studied by scanning tunneling microscopy at temperatures around 50 K. Hydrogen was found to adsorb dissociatively forming different ordered structures as a function of coverage. In order of increasing coverage θ in monolayers (ML) these were (√3×√3)R30° at θ = 0.3 ML; (2×1) at θ= 0.50 ML, (2×2)-3H at θ = 0.75, and (1×1) at θ = 1.00. Some of these structures were observed to coexist at intermediate coverage values. Close to saturation of 1 ML, H-vacancies (unoccupied three fold fcc hollow Ru sites) were observed either as single entities or forming transient aggregations. These vacancies diffuse and aggregate to form active sites for the dissociative adsorption of hydrogen.

Introduction

Understanding the chemical processes involved in the dissociative adsorption of H_2 on surfaces is important in a vast number of chemical processes, for example in Fisher-Tropsch and Ammonia Synthesis reactions [1]. Ruthenium is a good catalyst for these reactions and for reactions involving organic synthesis [2, 3]. Numerous studies have been devoted to determine the structures formed by hydrogen on Ru, particularly on its closed-packed hexagonal face [4-16]. All studies show that H_2 dissociates readily into H

atoms on Ru at all temperatures. The three-fold fcc-hollow site has been identified as the energetically favorable H binding site on Ru(001) at any coverage by *ab-initio* and Density Functional Theory (DFT) calculations [4, 5]. Recent and past experimental results using high resolution electron energy loss spectroscopy (HREELS) [6] and low energy electron diffraction (LEED) [7] generally agree with H fcc-hollow adsorption site although such preference was not found to be strong in other experimental studies [8-11]. As a function of coverage three ordered structures were observed by LEED [12]: (√3×√3), p(2×1) in 3 domains, and (2×2)-3H. Other experimental studies using HREELS and temperature programmed desorption (TPD) [6], [7], [11] agree with the later LEED study.

It was also found that both the adsorption and diffusion of hydrogen are strongly influenced by the presence of impurities such as CO [8, 9, 17], oxygen [6, 9] and carbon [9]. HREELS measurements suggested formation of CH [9], and in case of oxygen impurities it was suggested that O modifies the H adsorption site to the hcp-hollow [6].

To our knowledge the present study of hydrogen adsorption on Ru(001) is the first one carried out with Scanning Tunneling Microscopy (STM), a real space technique providing direct local information on the structures formed by hydrogen and the only one that permits to directly assess the role of impurities and defects. This is important because impurities present in concentrations below 1% of a monolayer (ML) are very difficult to ascertain with most other techniques. Our results illustrate the coexistence of several ordered structures at coverage values intermediate between those corresponding to the ideal (√3×√3)R30°, (2×1), (2×2)-3H, and (1×1) structures where the coverage is 0.33, 0.5, 0.75 and 1 monolayer (ML) respectively. While our STM study confirmed the results of a previous LEED study [12], we could also observe the formation and growth of small domains and the coexistence of phases, adding new information to help understand the important H-Ru system. In addition we were able to study local impurity effects and fundamental mechanism behind dissociative adsorption of hydrogen on Ru(001). Using high spatial resolution of STM we succeeded to unveil the nature of the active sites where dissociative adsorption of H_2 takes place near saturation coverage. Dissociation appears to require ensembles of three or more H-vacancies, in a similar way to the hydrogen dissociative adsorption on Pd(111) [18]. The structure and occurrence of

these ensembles is governed entirely by the dynamics of vacancy diffusion and aggregation. A detailed discussion of these dynamic effects is however outside of the scope of the present paper and will be presented in a separate publication [19].

2. Experimental

The experiments were carried out in an ultrahigh vacuum chamber with base pressure below 5×10^{-10} Torr (1 Torr = 1.33 mbar) equipped with several surface science characterization techniques, including Auger Electron Spectroscopy (AES), LEED, Ion Sputtering and Quadruple Mass Spectroscopy (QMS). The home made Scanning Tunneling Microscope (STM) consists of a sample stage mounted on a variable temperature liquid helium flow cryostat [20]. The STM head is attached to the sample stage by magnetic clamping, providing the same temperature on the sample and the scanning tip for higher resolution imaging. The tips were made of Pt/Rh30% and were prepared by electrochemical etching in a molten 1:4 solution of NaCl and $NaNO_3$.

The Ru(001) sample, in the shape of a disk, was prepared by noble gas ion bombardment while the sample was subjected to heating and cooling cycles from 550 K to 1100 K. After this process, the sample was cooled down to 50 K followed by a final rapid flash to 1100 K to remove surface contaminants accumulated during the initial slow cooling process. Heating was provided by electron beam bombardment from a thoriated tungsten filament located behind the sample. The sample temperature was measured with a Ni-Cr thermocouple. This preparation procedure produced a clean and well ordered surface with terraces larger than 100 nm. Adsorbed impurities, observed in the STM images as protrusions or depressions, were present in amounts less than 0.2 % of a ML while subsurface impurities, producing weak local changes in the atomic corrugation contrast (< 5 pm), were present in concentrations below 1 %.

The partial pressure of background hydrogen in the chamber measured by QMS was below 1×10^{-10} Torr. Hydrogen exposures were done by backfilling the chamber via a leak valve to pressures in the 10^{-9}-10^{-7} Torr range depending on the required H coverage.

3. Results and discussion

3.1 Clean Ru(0001)

After preparation the sample was checked for surface impurities by AES, which occasionally showed a very small oxygen peak, with an estimated coverage of 1 % or less. STM images revealed atomically flat terraces wider than 100 nm separated by monatomic steps. Our typical tunneling conditions were ±150mV bias, applied to the sample, and 300 pA tunneling current, corresponding to 500 MΩ impedance. The atomic corrugation of the Ru atoms was very small, less than a picometer under these conditions. Using lower gap resistances of 1.21 MΩ (40 mV, 33 nA) atomic resolution images with 3 pm corrugation such as that in Fig. 1a (with corresponding model in Fig. 1c) were obtained. These images were used to fine-tune the scanning distance calibration and to determine the crystal orientation used as a guide for further adsorption structure determination. It should be mentioned that study of increasing hydrogen adsorption coverage was done by consecutively scanning the same area of the Ru(001) surface. When adsorbates were present on the surface, tunneling conditions of high gap resistance were used to avoid tip interactions.

3.2 Low hydrogen coverage regime (<1/3 ML)

H_2 was admitted into the chamber to a pressure of 2×10^{-8} Torr for several seconds at a sample temperature of 54 K. The initial adsorption produces images (not shown) with streaks appearing in the timescale of the fast scanning, which we attribute to diffusing H atoms. The diffusion of hydrogen on Ru(001) was studied extensively in the past by Mak et al. [21-23]. The findings of these papers can be extrapolated to our temperature regime to give a diffusion coefficient value of $\sim5\times10^{-15}$ cm^2 s^{-1}, corresponding to a random walk distance of approximately 5 to10 lattice sites per second in the 54 K to 73 K temperature range. Such diffusion cannot be detected with our scanning speed of approximately 1minute per scan, explaining why isolated H atoms could not be observed.

As the concentration of H on the surface increased by additional exposure to the gas, diffusion stopped when large ordered islands formed (Fig. 1b). By comparison with the atomically resolved images of the clean Ru (Fig. 1a), the adsorbate periodicity, unit cell dimension and orientation could be established as a $(\sqrt{3}\times\sqrt{3})R30^{o}$ with one H atom per unit cell (Fig. 1d). The hydrogen atoms appear as depressions (the dark spots in the images) because of the lower tunnel probability, independent of bias voltage and sign in the range from -0.15 to +0.15 V. This is similar to the only other STM observations of hydrogen on metals [18, 24, 25]. Because the tunneling probability is higher over clean Ru, the areas not covered by hydrogen appear bright in the contrast images.

3.3 Intermediate hydrogen coverage (1/2 ML)

Continued exposure in 7×10^{-9} Torr of H_2 lead to the formation of a higher coverage structures with a (2×1) periodicity relative to the substrate. Three rotational domains with (2×1) periodicity following the three equivalent compact atomic rows of the substrate separated by 120^{o} were observed. Also, equivalent rotational domains were often observed separated by antiphase boundaries. In addition, as the coverage increased beyond 0.5 ML the (2×1) domains coexisted with domains of the next higher coverage, the (2×2)-3H structure described below. STM images (Fig. 2a and b) show two orientations of (2×1) phase (models in Fig. 2c and d) and also coexisting (2×2)-3H phase.

3.4 High coverage regime (3/4 ML)

As the sample continued to be exposed to H_2 gas at a background pressure of 7×10^{-9} Torr the domains of the (2×2)-3H phase shown in Fig. 3 grew and eventually covered the entire surface (Fig. 3a). Because of the low contrast over the H atoms (dark in the images), the (2×2)-3H phase in STM images (Fig.3a) shows up as (2×2) structure of bright spots corresponding to vacancies (Fig.3b). Near antiphase boundaries, as in the center of the image in Fig. 3a, the H atoms can hop to neighboring vacancy sites which produces the blurred spots that are visible in the image. After completion of the (2×2)-3H structure no significant changes were detected, indicating that at this coverage the dissociative hydrogen sticking coefficient dropped substantially.

This is related to the absence of contiguous vacancy ensembles where the hydrogen molecule can dissociate as discussed later and in another publication [19].

3.5 Near saturation coverage (≤ 1 ML)

In order to increase the coverage beyond 0.75 ML, the hydrogen pressure was increased to 1×10^{-7} Torr and the sample temperature to 73K. Under these conditions further dissociative H_2 adsorption took place giving rise to a new structure shown in Fig. 4a, which initially still contains many bright spots corresponding to H-vacancies. The new structure, which appears darker in comparison to the contrast of the H vacancies, has (1×1) periodicity and a local coverage of 1ML (Fig. 4c). Atomic corrugation of H in the (1×1) phase is very weak and barely visible in Fig. 4a. The number of vacancies decreases as additional hydrogen adsorbs until very few residual vacancies remain, as shown in Fig. 4b. The images also show some impurities that appear as dark spots surrounded by H vacancies (Fig. 4a and Fig. 4b). They are due to oxygen atoms, as deduced from examination of many images of Ru(001) that show that their number correlates with the O-signal in the AES. Oxygen appears as a depression in the STM images on most metals [26, 27, 28, 29].

As the H vacancies diffuse (slowly at this temperature), they occasionally come together in nearest neighbor sites and form aggregated ensembles of two or more vacancies. As observed previously in our laboratory on Pd(111) [18,24], aggregates of two or more vacancies appear as blurred triangular regions in STM images (Fig 5a), due to the rapid diffusion of hydrogen atoms exchanging place with vacancies inside triangular regions delimited by compact rows of H atoms. In the example of Fig. 5a we can see two triangular regions of sides equal to two and three ruthenium lattice distances, formed by two and three vacancy ensembles respectively as shown in the model (Fig. 5b). Such vacancy aggregates exist only for a limited time. After a few minutes they either separate back into individual vacancies or are filled with two H atoms from the dissociative adsorption of a hydrogen molecule, which annihilates two of the vacancies. In complete similarity to previous observations of H on Pd(111) [18] the dissociative adsorption of hydrogen on Ru(001) requires vacancy ensembles made of three or more hydrogen vacancies. A detailed and extensive account of

this formation of active sites for hydrogen dissociative adsorption near a complete monolayer coverage at 75 K on Ru(001) is presented in a separate publication [19].

4. Effect of oxygen impurities

Oxygen and carbon are typical surface impurities in Ru crystals. Past experiments have shown that they strongly influence the adsorption and diffusion of hydrogen [6, 9]. Since atomic oxygen chemisorbs on Ru(001) hcp-hollow sites [30], it was even suggested that O may force H to adsorb on the hcp-hollow site [6]. In addition HREELS measurements [9] for H adsorption on C contaminated Ru(001) suggested formation of CH.

Oxygen was found to be the main contaminant in the Ru(0001) crystal used in this study. Carbon contamination was removed by sputtering and by heating in oxygen environment. To avoid segregation of bulk carbon to the surface, heating was limited to 1100 K. This always led to a small residual amount of oxygen. This oxygen appears in the images as a depression (black spots in Fig. 4a and b), due to decreased tunneling distance, of about 25 pm at a gap resistance of 500 MΩ. When the concentration of O was around 2 to 5 % of ML patches of (2×2) oxygen structure were found, in agreement with previous results of oxygen on Ru [31, 32].

In the present study of H adsorption we found that the oxygen atoms attract and immobilize three vacancies forming a triangular arrangement as shown in model in Fig. 4d. The geometry of these structures corresponds to hydrogen and vacancies in fcc-hollow sites and O in hcp-hollow sites, as in the clean Ru surface [30]. The interesting observation is that in spite of the very high coverage of H, close to saturation, oxygen atom forbids the hydrogen atom taking six nearest fcc-hollow ruthenium sites. No OH groups were observed to form in any experiment, even after heating to 200K. For comparison the formation of OH (which is the rate limiting intermediate in the O plus H reaction to form water on Pd(111)) was not observed until the temperature reached 220K and above[33]. In that study [33] it was concluded that the recombination of O and H to form OH and H_2O occurred only at the steps with activation energy below 0.42 eV. More detailed study

of coadsorption effects of carbon and oxygen with hydrogen and water will be discussed in another publication [34].

Conclusions

The structures formed by dissociative adsorption of hydrogen on Ru(001) around 50K were studied by STM. In the topographic images the H atoms appear as 2-3 pm deep depressions. A number of ordered structures were found during the process of covering the surface with hydrogen up to one monolayer. At 50 K H_2 molecules dissociate readily on the surface producing atoms that diffuse rapidly and are observed only as streaks in the images acquired at a rate of one minute per image. As the H coverage increased an ordered $(\sqrt{3}\times\sqrt{3})R30^{o}$ structure with one hydrogen atom per unit cell was formed first, with local coverage of θ=0.33 ML. Between 0.5 and 0.7 ML, three ordered domains with (2×1) structure rotated by 120^{o} and local coverage of θ=0.5ML appeared. In addition to these rotational domains, many defects in the form of antiphase boundaries were observed. Even before completion of the (2×1) structure, a new phase with (2×2) periodicity is formed with a unit cell containing three H atoms and a local coverage of 0.75 ML. Beyond 0.75 ML coverage further dissociative adsorption of hydrogen required that the surface be heated to 75K to increase adsorbate mobility. In this manner the aggregation of H-vacancies into active sites was possible and only on these aggregates of vacancies a dissociative adsorption of hydrogen can occur.

The presence of O impurities on hcp hollow sites of the Ru surface affects the structure of ordered H phases. Oxygen appears surrounded by three nearest empty fcc-sites and three H vacancies. Interestingly, at 73 K, and in spite of the H-O proximity, no OH was observed.

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Figure Captions:

Fig. 1. STM images and corresponding schematic representations for clean Ru(001) and first hydrogen adsorption structure with (√3×√3)R30° symmetry.

(a) STM topographic image of clean Ru(001), 4×4 nm^2 size, acquired at 50 K after sputter-anneal cleaning cycles. Atomic resolution of Ru(001) is visible showing hexagonal lattice with 3-5 pm corrugation. Crystal orientations are defined marking crystal direction vectors [100] and [010] in the Bravais-Miller representation These orientations are used as a guide for further adsorption structure determination.

(b) STM topographic, 4×4 nm^2 size, image acquired shortly after exposure to H_2 gas up to 1/3 ML coverage. H atoms appear as 10 pm depressions, in the location of the dark spots. They form a periodic (√3x√3) structure rotated by 30° relative to the Ru lattice.

(c) Schematic model of the clean Ru(001) surface with corresponding crystal directions. Hexagonal lattice of white circles is a top layer of Ru(001) surface.

(d) Schematic model of the H structure corresponding to a √3×√3 phase. Small black circles in 3-fold hollow sites are H atoms in fcc-hollow sites. Underlying hexagonal lattice of light circles is the Ru(001) surface. Hydrogen atomic rows make 30° angle relative to the [100] direction of the surface.

Fig. 2. STM images obtained after H adsorption to about 0.5 ML. The surface contains a mixture of phases, including three domains of (2×1) and a (2×2) phase. They correspond respectively to the (2×1)-H with 1/2 ML local coverage and (2×2)-3H with 3/4 ML local coverage.

(a) STM topographic image, 5×5 nm^2 in size, showing a structure of bright and dark rows in the upper part of the image and a (2×2) structure of bright spots at lower right corner. A line has been drawn at the

approximate location of the phase boundary. Bright spots are the location of H vacancies with a 20-25 pm corrugation.

(b) STM topographic image, $4\times4nm^2$ in size. Two separate phases of (2×1)-1H with 1/2 ML local coverage are visible in the right part of the image and a (2×2)-3H with 3/4 ML local coverage can be seen at lower left corner of the image.

(c) Schematic model of one of the (2×1)-1H phase. Underlying hexagonal lattice of light circles is the Ru(001) and small black circles in 3-fold hollow sites are H atoms in fcc-hollow sites. This phase consists of rows of hydrogen atoms in [110] direction which make 60° angle with [100] vector.

(d) Schematic model of the second (2×1)-1H phase. Underlying hexagonal lattice of light circles is the Ru(001) and small black circles in 3-fold hollow sites are H atoms in fcc-hollow sites. This phase consists of rows of hydrogen atoms in [010] direction which make 120° angle with [100] vector.

Fig. 3. STM image acquired after an exposure to hydrogen at a pressure of 7×10^{-9}Torr. Images reveal (2×2)-3H phase with 3/4 ML local coverage.

(a) STM topographic image, 4×4 nm^2 in size. A (2×2) structure of bright spots is observed with a 20-25 pm corrugation. This structure corresponds to (2×2)-3H phase with 3/4 ML local coverage. The bright spots correspond to H-vacancies and the hydrogen atoms are located in the dark spots. The fuzzy spots at the center of the image are caused by H atoms hopping between vacancies at the boundary line between antiphase domains.

(b) Schematic representation of (2×2)-3H structure on Ru hexagonal closed-packed surface. Where white circles forming hexagonal lattice correspond to Ru(001), small black circles in 3-fold hollow sites are H atoms in fcc-hollow sites and grey circles represent 3-fold fcc-hollow sites without hydrogen (H-vacancy), which shows up as bright (high tunneling probability) in actual STM contrast images. In lower right corner, the primitive cell of the structure is shown. Primitive cell contains three H atoms shown as small grey circles.

Fig. 4. STM images acquired after increased exposure of hydrogen (background pressure 1×10^{-7} Torr). The number of hydrogen vacancies decreases and 1×1 structure of H grows with 1ML local coverage. Oxygen impurity atom appears as a 30 pm depression (black dot) surrounded by three 25 pm protrusions (H vacancies). Thus oxygen forbids hydrogen atom from adsorbing at nearest six fcc-hollow sites.

(a) $4\times4nm^2$ STM topographic image at a H coverage above 3/4ML. To increase the coverage above 3/4 ML the hydrogen background pressure was increased to 1×10^{-7} Torr and the sample temperature from 50 K to 73 K. Bright spots correspond to H vacancies surrounded by a darker area that shows a very week 2-3 pm corrugation. This area corresponds to a saturated (1×1) structure of hydrogen with 1 ML local coverage. One type of impurity is observed as dark 30 pm depressions surrounded by three bright spots. This impurity is O atom surrounded by H vacancies (bright spots), forming a triangle with the orientation corresponding to the orientation of hcp-hollow site.

(b) 3×3 nm^2 STM topographic image at a H coverage closer to 1 ML. The (1×1) H periodicity is visible with corrugation of 2-3 pm. Three residual isolated H vacancies are still present in this image as well as one oxygen atom (black spot) impurity surrounded by three H vacancies (three bright spots).

(c) Schematic model of the (1×1)-1H phase. Underlying hexagonal lattice of light circles is the Ru(001) surface and small black circles in 3-fold hollow sites are H atoms in fcc-hollow sites. This phase consists of saturated one monolayer of hydrogen on Ru(001).

(d) Schematic model of the oxygen impurity (black circle) surrounded by three hydrogen vacancies (grey circles). Thus oxygen impurity atom forbids hydrogen adsorption on nearest six fcc-hollow sites. Underlying hexagonal lattice of light circles is the Ru(001) surface and small black circles in 3-fold hollow sites are H atoms in fcc-hollow sites.

Fig. 5. STM images acquired at 1ML hydrogen coverage during formation of two H-vacancy triangular aggregates.

(a) STM topographic image of the Ru surface covered by nearly 1 ML of hydrogen. A few residual H-vacancies are visible (bright spots) as well as two fuzzy triangular regions of two and three ruthenium lattice distances by side. They are aggregates of 2 and 3 H-vacancies exchanging positions with H atoms inside the equilateral triangle. Depending on the number of vacancies aggregated the size of the triangles change, but always maintains the same orientation relative to the substrate Ru lattice. With time the aggregates separate into isolated vacancies or, in the presence of gas phase H_2, dissociatively adsorb a molecule that decreases the number of vacancies by two.

(b) Schematic representation of two triangular aggregates of H-vacancies of two and three ruthenium lattice distance size by side. Underlying hexagonal lattice of light circles is the Ru(001) surface and small black circles in 3-fold hollow sites are H atoms in fcc-hollow sites. Grey circles represent single H vacancies. Dashed line triangles represent H vacancies aggregates of triangular shape. Upper triangular aggregate is formed of two H vacancies and lower triangular aggregate is formed of three H vacancies. The orientation of all triangular vacancy aggregates is the same as of fcc-hollow site. H atoms inside the vacancy aggregates (dashed line triangle) move considerably fast from one fcc-hollow site to the others inside triangle via bridge sites (as shown by the dotted line) not allowing STM to reveal them as single entities. Instead the area where hydrogen moves inside aggregates appears as fuzzy triangular area in STM images.